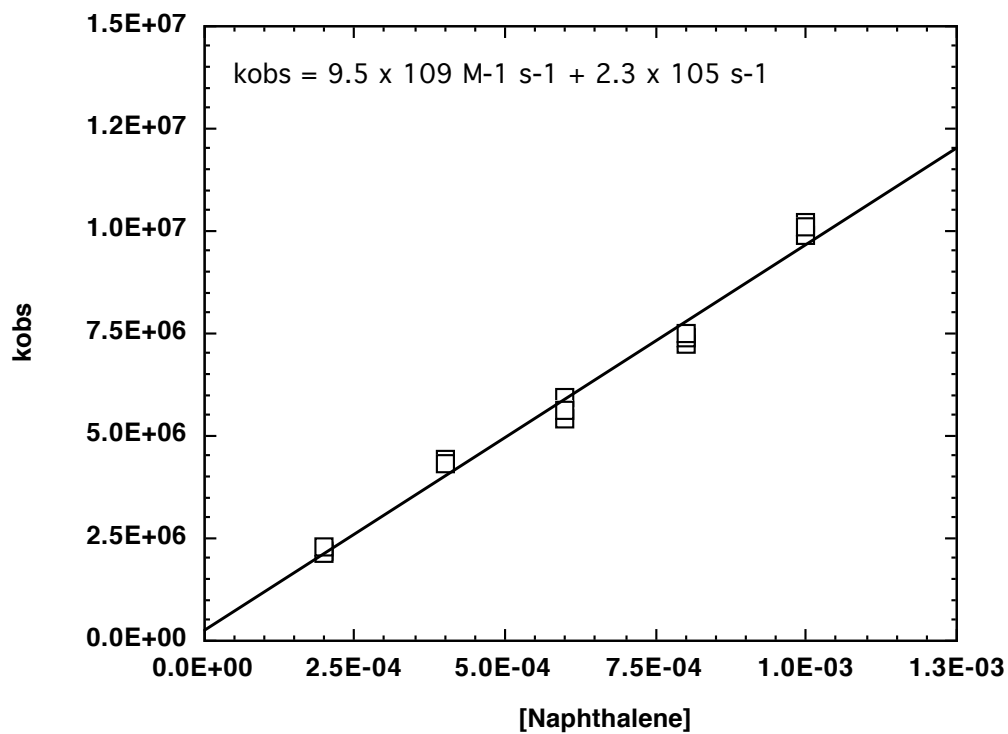


Question 1.

$$k_q = 9.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

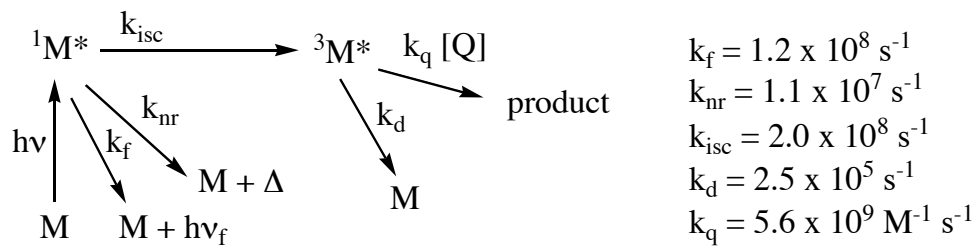
decay rate at zero [naphthalene] = $2.3 \times 10^5 \text{ s}^{-1}$, therefore lifetime = $4.34 \mu\text{s}$.

$$k_{\text{diff}} \sim 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$



This rate constant is close to the diffusion controlled limit, as expected for exothermic triplet-triplet energy transfer

Question 2.



$$\Phi_f = k_f / (k_f + k_{nr} + k_{isc}) = 0.362$$

$$\Phi_{\text{prod}} = \Phi_{\text{triplet}} \cdot \Phi_{\text{prod}}^{\text{triplet}}$$

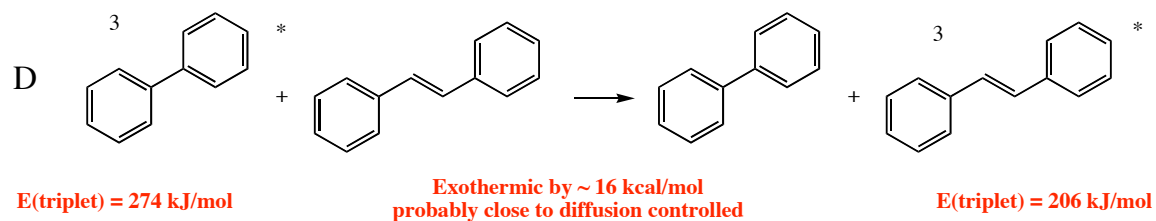
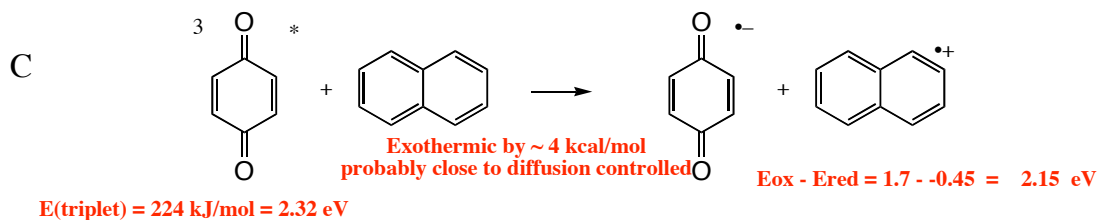
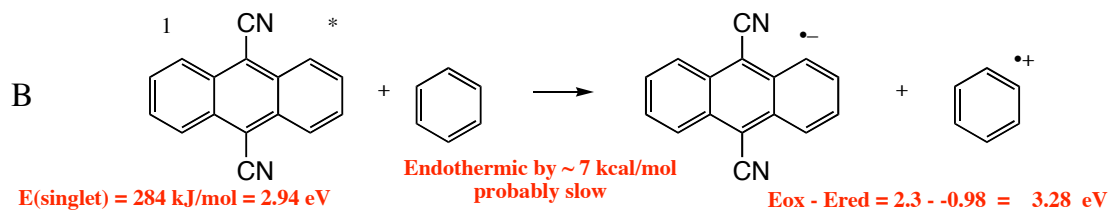
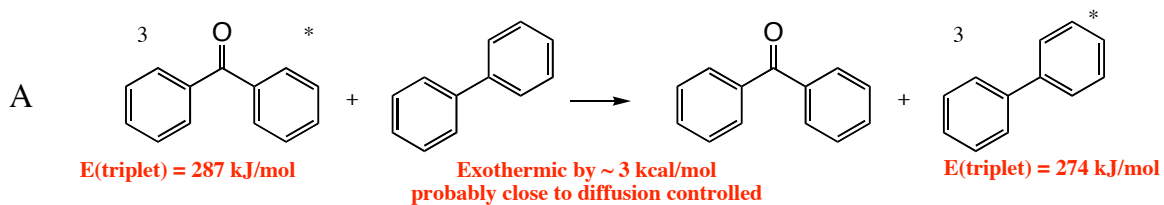
$$\Phi_{\text{prod}} = k_{isc} / (k_f + k_{nr} + k_{isc}) \cdot k_q [Q] / (k_q [Q] + k_d)$$

$$\Phi_{\text{prod}} = 0.604 \cdot 0.818 = 0.494$$

$$\Phi_{\text{prod}}^{\text{max}} \sim \Phi_{\text{triplet}} = 0.604$$

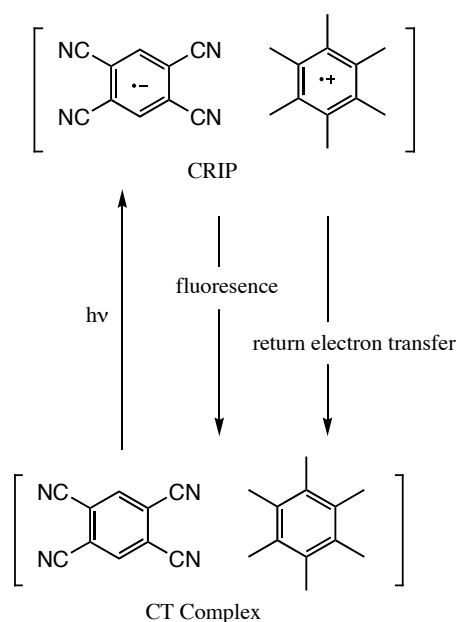
The quantum yield in the limit of infinite concentration of quencher is essentially the same as the quantum yield for formation of the triplet. Note that (essentially) all of the triplets give products, but not all of the singlets give triplets, so the yield is still not unity.

Question 3.



Question 4.

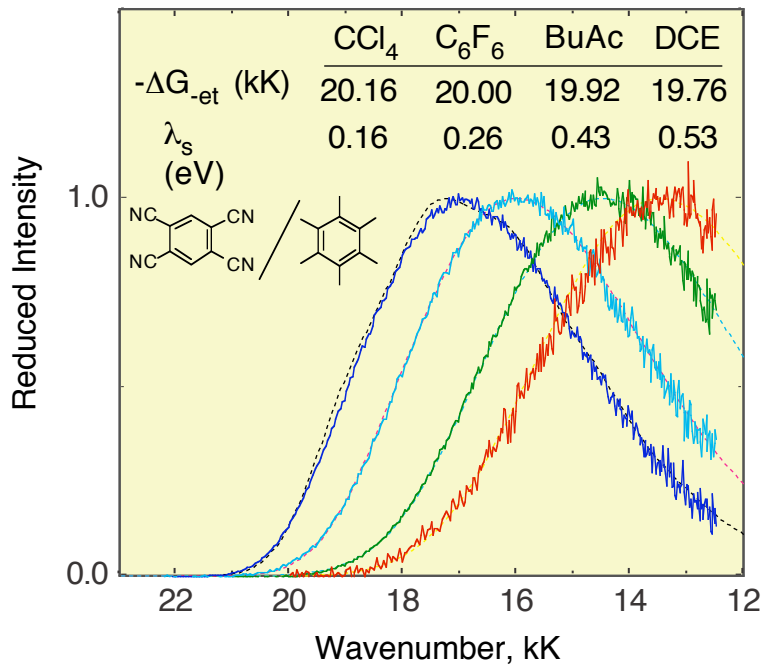
The question comes from our paper, Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. "Radiative and Nonradiative Electron Transfer in Contact Radical-Ion Pairs" *Chem. Phys.* **1993**, *176*, 439. The data relates to:



Excitation of the CT complex gives the CRIP. The CRIP both fluoresces (although rather weakly) but mainly undergoes return electron transfer. The rate of return electron transfer is calculated using the usual Golden Rule expression. We determined the matrix element to be 800 cm^{-1} (come and ask me how we did that if you like). The FCWD for the return electron transfer depend upon the usual parameters, $\Delta E_{0,0}$, λ_s , λ_v etc. In this case, $\Delta E_{0,0} = \Delta G_{-et}$, i.e. the energy of the excited state is the free energy of the return electron transfer reaction. These parameters are quite different for different CRIP and for the same CRIP in different solvents, due to the fact that the CRIP is more stabilized in more polar solvents and has a larger λ_s in more polar solvents. The question is how to determine the FCWD parameters?

The answer lies in the (weak) emission. The bandshapes of the emission spectra are determined by the same FCWD that are involved in the return electron transfer reactions. All you need to do is determine the values of these parameters required to fit the spectra (this is what you did), then use these parameters to determine the rate constant for a corresponding electron transfer reaction that had the same values of the parameters (this is what the program did for you).

The values given in our paper for the fits to these spectra are shown in the Figure and table below (the fits shown in the figure are to the reduced spectra):



	$\Delta E_{0,0}$ (= ΔG_{-et})	λ_s	k_{Calc}	k_{Expt}
CCl ₄	2.50 eV	0.16 eV	$2.1 \times 10^7 \text{ s}^{-1}$	$3.8 \times 10^7 \text{ s}^{-1}$
TCE	2.52 eV	0.35 eV	$2.6 \times 10^8 \text{ s}^{-1}$	$3.5 \times 10^8 \text{ s}^{-1}$
CHCl ₃	2.43 eV	0.44 eV	$2.2 \times 10^9 \text{ s}^{-1}$	$2.0 \times 10^9 \text{ s}^{-1}$

Zofia got:

CCl ₄	2.50 eV	0.16 eV	$2.0 \times 10^7 \text{ s}^{-1}$	$3.8 \times 10^7 \text{ s}^{-1}$
TCE	2.52 eV	0.35 eV	$2.3 \times 10^8 \text{ s}^{-1}$	$3.5 \times 10^8 \text{ s}^{-1}$
CHCl ₃	2.41 eV	0.42 eV	$1.8 \times 10^9 \text{ s}^{-1}$	$2.0 \times 10^9 \text{ s}^{-1}$

David got:

CCl ₄	2.77 eV	0.42 eV	$3.7 \times 10^7 \text{ s}^{-1}$	$3.8 \times 10^7 \text{ s}^{-1}$
TCE	2.52 eV	0.42 eV	$2.2 \times 10^8 \text{ s}^{-1}$	$3.5 \times 10^8 \text{ s}^{-1}$
CHCl ₃	2.41 eV	0.42 eV	$1.9 \times 10^9 \text{ s}^{-1}$	$2.0 \times 10^9 \text{ s}^{-1}$

Jaswinder and Pallav got:

CCl ₄	2.65 eV	0.31 eV	$2.7 \times 10^7 \text{ s}^{-1}$	$3.8 \times 10^7 \text{ s}^{-1}$
TCE	2.60 eV	0.43 eV	$2.9 \times 10^8 \text{ s}^{-1}$	$3.5 \times 10^8 \text{ s}^{-1}$
CHCl ₃	2.41 eV	0.41 eV	$1.6 \times 10^9 \text{ s}^{-1}$	$2.0 \times 10^9 \text{ s}^{-1}$

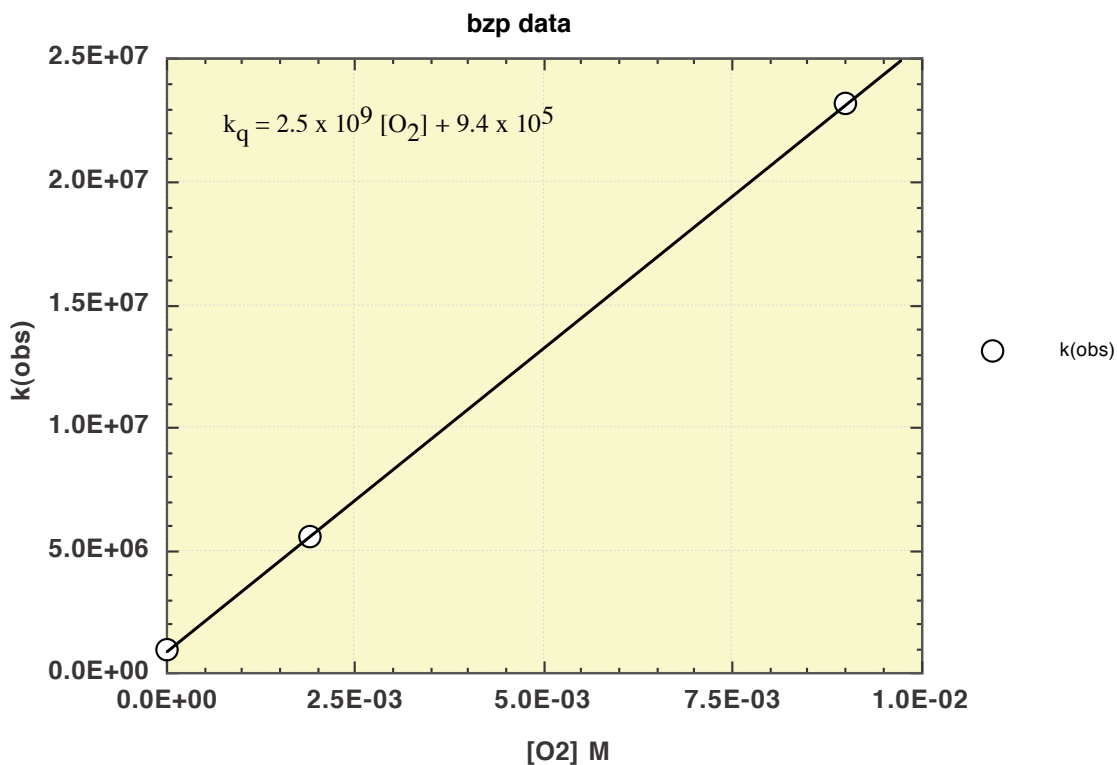
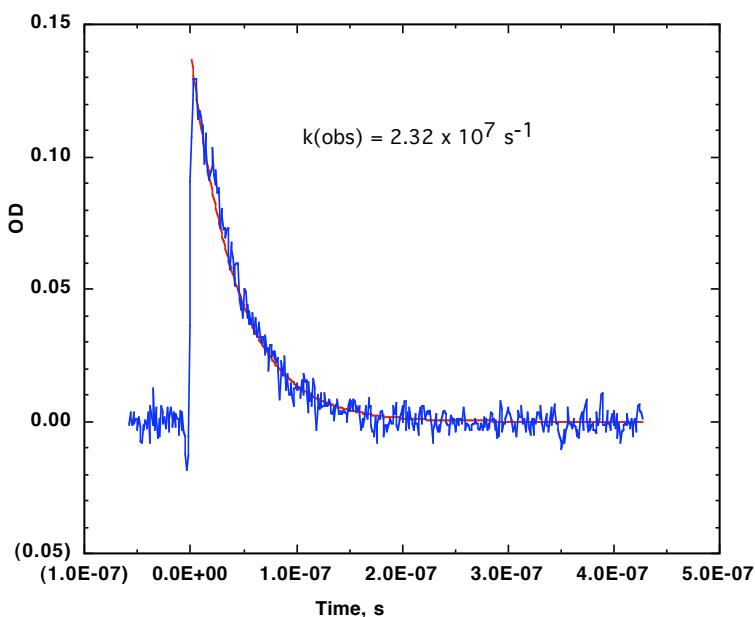
Carola got:

CCl ₄	2.75 eV	0.41 eV	$2.4 \times 10^7 \text{ s}^{-1}$	$3.8 \times 10^7 \text{ s}^{-1}$
TCE	2.55 eV	0.38 eV	$1.7 \times 10^8 \text{ s}^{-1}$	$3.5 \times 10^8 \text{ s}^{-1}$
CHCl ₃	2.43 eV	0.44 eV	$1.3 \times 10^9 \text{ s}^{-1}$	$2.0 \times 10^9 \text{ s}^{-1}$

If you compare the calculated (in blue) and experimental rate constants (in red), you will see remarkable agreement between calculated (from the parameters used to fit the spectra) and experimentally measured return electron transfer rate constants. This agreement between predicted and experimental rate constants was considered to be important in confirming that the electron transfer theory problem (in solution at least) was essentially solved.

Question 5.

Here is an exponential fit to the decay data. I got a first order rate constant of $2.3 \times 10^7 \text{ s}^{-1}$.



Here is the rate plot, the bimolecular rate constant is obtained as the slope of this plot. I got a value of $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The diffusion controlled rate in acetonitrile is ca. $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. In this case the measured rate constant is ca. 1 order of magnitude smaller than the diffusion limit. This is expected, and we will talk about why this is in lecture later in the semester.

Question 7.

The commonly used dimensions for the various parameters are:

This is an interaction energy. If h is used in J s, then this energy has to be in J too!

$$k = \frac{4\pi^2}{h} V^2 \text{ FCWD}$$

to make everything balance, this has to be in J⁻¹, i.e. it is a number (density of states) per unit energy.

$$V = 500 \text{ cm}^{-1} = 9.93 \times 10^{-21} \text{ Joules (note, do not use joules per mole!)}$$

$$k = \frac{4\pi^2}{h} V^2 \text{ FCWD}$$

$$\text{FCWD} = \frac{k h}{4\pi^2 V^2} = \frac{6.626 \times 10^{-34} \times 1.7 \times 10^7}{39.48 (9.93 \times 10^{-21})^2}$$

$$= \frac{1.126 \times 10^{-26}}{3.89 \times 10^{-39}} = 2.89 \times 10^{12} \text{ J}^{-1}$$

The units of FCWD are thus energy⁻¹. In the case above, the equation was solved in energy units of J, thus the FCWD is a density of states per Joule.